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(54) Title: TETRABLOCK COPOLYMERS

(57) **Abstract:** This invention relates generally to linear tetrablock copolymer compositions and their use in road-marking applications. These tetrablock copolymers contain polystyrene, polyisoprene and polybutadiene components. Road-marking compounds prepared from these copolymers further contain a hydrocarbon resin or rosin ester or both. These block copolymer are readily mixed using melt-mixing techniques, thus, avoiding both powder grinding and high-shear stirring.

TITLE: TETRABLOCK COPOLYMERS**FIELD**

5 This invention relates generally to linear tetrablock copolymer compositions and their use in road-marking applications. These tetrablock copolymers contain polystyrene, polyisoprene and polybutadiene components. Road-marking compounds prepared from these copolymers typically further contain hydrocarbon resin, fillers and glass beads.

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BACKGROUND

Block copolymers are generally known in the art and have been used in a variety of applications. There are two basic, distinct block copolymer types: linear and radial.

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Radial block copolymers contain polymer block branches radiating from a central coupling agent. Such polymers are described in, for example, U.S. Patent No. 5,399,627. This patent describes polymers for use in pressure sensitive adhesive compositions and describes radial block copolymers comprised of polystyrene, polyisoprene, and polybutadiene block segments.

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Linear block copolymers do not have radiating branches; the block components are arranged sequentially. For example, U.S. Patent No. 5,750,623 describes linear styrene-isoprene-styrene and styrene-butadiene-styrene block copolymers useful in hot-melt adhesives.

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Linear block copolymers are also used to prepare compositions for road or pavement marking. Such compositions typically comprise copolymer elastomer and hydrocarbon resin components as well as color and reflective additives such as pigments and glass beads.

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U.S. Patent No. 5,213,439 is directed to pavement marking and describes a dry-blended powder containing linear or radial tri-block copolymers with two poly(vinylaromatic) blocks and a conjugated diene block. This copolymer must be ground to a powder before mixing with hydrocarbon resins and other additives. This grinding replaces prolonged melt-blending procedures using expensive high-shear stirring to mix thermoplastic rubbers with hydrocarbon resin.

We have discovered that certain linear tetrablock copolymer compositions are readily melted and mixed with hydrocarbon resin thus avoiding both powder grinding and high-shear stirring. Such copolymers have potential value in road-marking applications in addition to their more typical adhesive applications.

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SUMMARY

The present invention relates to a tetrablock copolymer composition comprising a linear SISI or SISB block copolymer. The block copolymers are of styrene and isoprene and/or butadiene. The styrene content of the polymers used in the present invention should be from 10–27 percent by weight, alternatively from 12–20 or 15–18 percent by weight.

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Molecular weights are measured by Gel Permeation Chromatography (GPC), where the GPC system has been appropriately calibrated for example by using standards of similar known-molecular-weight polymer.

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Accordingly, the present invention selects polymers that enable good melting when mixed in traditional thermoplastic road-marking mixers. Some polymer embodiments have the following properties: an overall styrene content between 10–27 wt%, alternatively between 12–20 wt%. The preferred rubbers are 100% tetrablock.

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The styrenic block copolymers used in some invention embodiments have a molecular weight of from 45,000–250,000. The molecular weights of the various copolymer blocks may be varied. Some embodiments select the styrenic blocks with a molecular weight of from 4,000–35,000, alternatively, 6,000–20,000 or 8,000–20,000.

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The unsaturated diene blocks should have a molecular weight of from 10,000–200,000, alternatively, 10,000–150,000 or 10,000–50,000 which is particularly preferred with isoprene blocks. Unsaturated diene blocks with molecular weights of 20,000 or above provide a suitably strong polymer. Unsaturated diene blocks with molecular weights of 200,000 or less are suitably processable. Where SISI, SISB, SBSI, or SSSB polymers are used, the molecular weight of the two unsaturated diene blocks can be varied.

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DETAILED DESCRIPTION

This invention's linear tetrablock copolymers are particularly useful in road-marking compounds due to their flowability and quick melting capability. They can easily be melt mixed with hydrocarbon resins and other additives without powdering or high-shear mixing. Each block may be either polystyrene (S), polybutadiene (B), or polyisoprene (I). Since there must be four blocks, one of the blocks will be repeated. In some embodiments, the tetrablock copolymer contains two S blocks plus two B blocks, two I blocks, or one B and one I block, i.e.: S-I-S-I, S-I-S-B, S-B-S-B and S-B-S-I.

Each block is present at 10–90 wt% of block copolymer based on the total copolymer weight. In some embodiments, an S component exists in a tetrablock copolymer at a minimum of 5 wt%, alternatively, a minimum of 10 wt%. The S component exists at up to 70 wt%, alternatively up to 60 wt%, up to 40 or up to 30 wt% of the copolymer.

The weight-average molecular weight of invention tetrablock copolymers varies widely depending on the copolymer's make-up. Generally, the overall peak weight-average molecular weight has a minimum of 10,000, alternatively, a minimum of 50,000, or 100,000. The overall peak weight-average molecular weight maximum is 1,000,000, alternatively not more than 500,000, not more than 300,000, or not more than 200,000.

In some embodiments, the invention linear tetrablock copolymers are "pure" in the sense that they contain no measurable residual triblock or diblock copolymer. But they may contain up to 1% by weight residual triblock and/or diblock copolymer.

For road-marking application, these linear tetrablock copolymers are mixed with a hydrocarbon resin, such as a substantially non-aromatic hydrocarbon resin, or with a rosin ester or a blend of both. Substantially non-aromatic means that if there is aromatic hydrocarbon present, it is at a low enough level to function in these copolymer compositions. Preferred non-aromatic resins are polymerized from a stream of aliphatic petroleum derivatives in the form of dienes and monoolefins containing 5 to 6 carbon atoms. At room temperature, these hydrocarbons range from materials that are normally liquid to those that are normally solid at

room temperature. Commercially available resins, such as ESCOREZ™ 1102RM (ExxonMobil Chemical), are suitable. Many useful resins have a Ring and Ball softening point (ASTM D 28-96) from 90–110°C, alternatively from 95–105°C, and a melt viscosity at 160°C (ETM-E-31) from 500–3000 mPa sec, alternatively from 1000–2500 mPa sec. Suitable hydrocarbon resins are well known and commercially available, e.g. under the trademarks "ESCOREZ™", "HERCULES™", "QUINTONE™". Suitable rosin esters are commercially available, e.g. under the trademarks "BEVILINE™" and "SYLVATAC™".

The relative amounts of tetrablock copolymer and hydrocarbon resin depends on the selected components. Typically, the block copolymer and hydrocarbon resin are present in a weight ratio of from 0.5:99.5 to 20:80, preferably from 2:98 to 15:85.

Invention road-marking compositions may further contain additives such as pigments, glass beads, fillers, oils, and viscosity modifiers. Titanium dioxide is a particularly useful pigment, and mineral aggregates are particularly useful fillers.

The compositions' individual components may be combined in a number of ways, but the invention copolymers are uniquely suited to simple melt mixing with the hydrocarbon resin and any desired additive. Typically, the melt-mixing temperature has a minimum of 170°C or 180°C. Typically, the maximum melt-mixing temperature is 200°C, but melt-mixing temperatures as high as 210°C are not unusual.

The tetrablock copolymers may be prepared by any suitable polymerization technique. Polymerization systems in which the blocks are produced sequentially are preferred to those in which two or more pre-formed blocks are coupled to each other. The preferred, sequential, polymer development enables greater variation in the molecular weight of the blocks.

EXAMPLES

The following examples are intended to illustrate the melt behavior of invention tetrablock copolymers as compared to triblock and diblock copolymers. The samples were placed in an oven at 190 °C for 5 and 10 minutes. Faster

melting and higher flowability indicate that the polymer will be easier to mix for road-marking applications.

The molecular weights reported here are peak molecular weight as measured by size exclusion chromatography using polystyrene calibration. Commercially available polystyrene standards were used for calibration, and the molecular weights of copolymers corrected according to Runyon et al, *Journal of Applied Polymer Science*, Vol. 13, Page 359 (1969) and Tung, L. H., *Journal of Applied Polymer Science*, Vol. 24, Page 953 (1979).

Typically, the melt-mixing temperature has a minimum of 170 °C or 180 °C. The maximum melt-mixing temperature is usually 200 °C, but melt-mixing temperatures as high as 210 °C are not unusual.

Melt flow rate (MFR) was determined using ASTM D 1238, 200/5.0.

Comparative Sample 1 is an S-I-S triblock copolymer, VECTOR™ 4111 (commercially available from Dexco Polymers).

Comparative Sample 2 is an S-I-S/S-I triblock/diblock copolymer mix, VECTOR™ 4113 (commercially available from Dexco Polymers).

Comparative Sample 3 is an S-I-S/S-I triblock/diblock copolymer mix, VECTOR™ 4114 (commercially available from Dexco Polymers).

Comparative Sample 4 is an S-I-S/S-I triblock/diblock copolymer mix, DPX 559™, (commercially available from Dexco Polymers) having 15% styrene, 55% SI and a Melt Flow Rate (condition G) of 44 g/ 10 min.

Comparative Sample 5 is an S-I-S triblock copolymer, DPX 562™ (commercially available from Dexco Polymers). DPX 562™ is a linear SIS with 15% styrene and a Melt Flow Rate (ASTM 1238, 200/5.0) of 25 g/10 min.

Comparative Sample 6 is an S-I-S/S-I triblock/diblock copolymer mix, DPX 565™ (commercially available from Dexco Polymers). DPX 565™ has the following properties. Molecular weight SIS: 176000 g/mol; Molecular weight SI: 83000 g/mol; Styrene content SIS: 16.1% (by weight); Styrene content SI: 16.1% (by weight); SI content: 54% of the polymer.

Invention Sample 7 is an S-I-S-I tetrablock copolymer in accordance with this invention made at Dexco Polymers by sequential polymerization. It has the

following respective molecular weights, in g/mol: 12400, 60000, 12400, 70000, and styrene content of 16% (by weight).

Invention Sample 8 is an invention S-I-S-B tetrablock copolymer made at Dexco Polymers by sequential polymerization. It has the following respective molecular weights, in g/mol: 11000, 57000, 11000, 40000, and styrene content of 19% (by weight).

Comparative Sample 9 is an S-I-S/S-I triblock/diblock copolymer mix, TR 1107TM (commercially available from Shell Oil Company).

Comparative Sample 10 is an S-I-S/S-I triblock/diblock copolymer mix, KRATONTM D 601 P (commercially available from Shell Oil Company).

Comparative Sample 11 is an S-I-S/S-I triblock/diblock copolymer mix, KRATONTM D 113 (commercially available from Shell Oil Company).

Comparative Sample 12 is an S-I-S/S-I triblock/diblock copolymer mix, QUINTACTM 3433 (commercially available from Nippon Zeon).

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Table 1

Sample	Melt Rating @ 5 min.*	Melt Rating @ 10 min.	% Styrene	% Diblock	MFR	MW
Comp.1	1	2	18	0	12	118000
Comp 2	2	4	15	18	10	154000
Comp 3	2	4	18	42	25	156000
Comp 4	2	5	15	58	37	162000
Comp 5	2	5	15	0	25	n/a
Comp 6	1	2	16	54	12	176000
Inv. 7	2	5	16	0		154000
Inv. 8	4	5	19	0		126000
Comp 9	2	4	15	17	9	n/a
Comp 10	3	4	15	19	12	n/a
Comp 11	2	4	16	56	16	168000
Comp 12	2	4	17	55	12	172000

*1=no change in sample; 2=sample slightly melted; 3=sample completely melted, no flow;
4=sample completely melted, limited flow; 5=sample completely melted good flow.

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While certain representative embodiments and details have been provided to illustrate the invention, it will be apparent to skilled artisans that various process and product changes from those disclosed in this specification may be made without departing from this invention's scope, which the appended claims define. These are within the scope of the invention. Furthermore, certain features or elements are described in the disclosure (i.e. specification and claims as filed).

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All combinations of these elements or features are within the invention's scope to the extent that the combinations do not conflict with the disclosure taken as a whole.

5 All patents, test procedures, and other documents cited in this specification are fully incorporated by reference to the extent that this material is consistent with this specification and for all jurisdictions in which such incorporation is permitted.

All documents to which priority is claimed are fully incorporated by reference for all jurisdictions in which such incorporation is permitted.

10 Certain invention features are described as numerical ranges or upper limits or lower limits. The invention specifically encompasses values of those features that fall between any of the specifically mentioned upper or lower limits unless otherwise indicated.

15 The specification and claims as filed disclose different aspects of the invention. The individual components or elements may be combined in any novel combination, regardless of whether the claims recite each individual combination, and remain within Applicants' intended disclosure.

CLAIMS

1. A road-marking compound comprising:
 - (a) at least one linear tetrablock copolymer having four blocks independently selected from polystyrene (S), polyisoprene (I) and polybutadiene (B); and
 - (b) at least one of hydrocarbon resin, rosin ester, or a mixture of rosin ester and hydrocarbon resin.
- 10 2. The road-marking compound of claim 1 wherein two of the blocks are the same and are one of polystyrene (S), polyisoprene (I), or polybutadiene (B).
- 15 3. The road-marking compound of claim 1 wherein the tetrablock copolymer is represented by the formula S-I-S-B, S-I-S-I, S-B-S-B or S-B-S-I wherein S is polystyrene, I is polyisoprene, and B is polybutadiene.
- 20 4. The road-marking compound of claim 3 wherein each of the four blocks is present in the amount of 10–90% wt% based on the total copolymer weight.
5. The road-marking compound of claim 4 wherein the copolymer's overall peak weight-average molecular weight ranges from 10,000–1,000,000.
- 25 6. The road-marking compound of claims 1–5 wherein the copolymer contains less than 1 wt% residual diblock.
7. The road-marking compound of claims 1–5 wherein the copolymer contains less than 1 wt% residual triblock.

8. The road-marking compound of claims 1-5 wherein the copolymer contains less than 1 wt% residual S-I diblock and less than 1 wt% residual S-I-S triblock.
- 5 9. The road-marking compound of claim 8 wherein the total residual S-I diblock and S-I-S triblock copolymer is less than 1 wt%.
- 10 10. The road-marking compound of claims 1-5 or 8 wherein the hydrocarbon resin is substantially non-aromatic.
11. The road-marking compound of claims 1-5 or 10 wherein the hydrocarbon resin viscosity is from 0.1–10 Pa sec at 160 °C.
12. The road-marking compound of claims 1-5, 8, 10, or 11 wherein the hydrocarbon resin softening temperature is at least 90°C.
- 15 13. The road-marking compound of claims 1-5, 8, 10, or 12 wherein the copolymer and hydrocarbon resin are present in a weight ratio of from 0.5:99.5 to 20:80.
- 20 14. A road-marking compound comprising:
 - (a) a linear tetrablock copolymer represented by the formula S-I-S-B, S-I-S-I, S-B-S-B or S-B-S-I wherein S is a polystyrene component, I is a polyisoprene component, and B is polybutadiene component; wherein each copolymer component is present in the amount of 10–90% wt% based on the total copolymer weight; the overall peak, weight-average molecular weight of the copolymer ranges from 10,000–1,000,000; and the copolymer contains less than 10 wt% residual S-I diblock and less than 10 wt% residual S-I-S triblock ; and

(b) a substantially non-aromatic hydrocarbon, having a viscosity ranging from 0.1–10 Pa sec, a wax cloud point of up to 190°C, and a softening point that is at least 90°C;

5 wherein the copolymer and hydrocarbon resin are present in a weight ratio of from 0.5:99.5 to 20:80.

10 15. A tetrablock copolymer composition comprising a linear block copolymer represented by the formula S-I-S-B wherein the S component is polystyrene, the I component is polyisoprene and the B component is polybutadiene.

15 16. The copolymer of claim 15 wherein the S component is present in the amount of 10–90 wt% of the block copolymer based on the total weight of the block copolymer.

17. The copolymer of claim 15 wherein the I component is present in the amount of 10–90 wt% of the block copolymer based on the total weight of the block copolymer.

20 18. The copolymer of claims 15-17 wherein the B component is present in the amount of 10–90 wt% of the block copolymer based on the total weight of the block copolymer.

19. The copolymer of claim 18 wherein

25 (a) the S component is present in the amount of 10–90 wt% of the block copolymer based on the total weight of the block copolymer;

(b) the I component is present in the amount of 10–90 wt% of the block copolymer based on the total weight of the block copolymer, and

30 (c) the B component is present in the amount of 10–90 wt% of the block copolymer based on the total weight of the block copolymer.

20. The copolymer of claim 19 wherein the overall, peak weight-average molecular weight of the copolymer is 10,000–1,000,000.
21. The copolymer of claim 20 wherein the copolymer contains less than 10 wt% residual S-I diblock.
5
22. The copolymer of claim 21 wherein the copolymer contains less than 10 wt% residual S-I-S triblock.
- 10 23. The copolymer of claim 22 wherein the copolymer contains less than 10 wt% residual S-I diblock and less than 10 wt% residual S-I-S triblock.
24. The copolymer of claim 15 wherein the copolymer contains less than 10 wt% residual S-B diblock.
15
25. A tetrablock copolymer composition comprising:
 - (a) A linear block copolymer represented by the formula S-I-S-B wherein
 - (i) the S component is polystyrene and is present at 10–90 wt% based on the total copolymer weight,
 - (ii) the I component is polyisoprene and is present at 10–90 wt% based on the total copolymer weight, and
 - (iii) the B component is polybutadiene and is present at 10–90 wt% based on the total copolymer weight20 wherein the overall peak weight-average molecular weight of the copolymer ranges from 200,000–1,000,000; and the copolymer contains less than 10 wt% residual S-I diblock, less than 10 wt% residual S-I-S triblock, and less than 10 wt% residual S-B diblock.
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- 30 26. A method of using any of the road-marking compounds of Claims 34-46 comprising supplying the tetrablock copolymer.

INTERNATIONAL SEARCH REPORT

I onal Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08L53/02 C08F297/04 C09D5/00 E01F9/04 E01F9/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08L C09D C09J E01F C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

° Special categories of cited documents :

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- *&* document member of the same patent family

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INTERNATIONAL SEARCH REPORT

International Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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